

# Molecular structures and charge-transfer complexes of *cis*-dibenzo[*c,h*]-1,6-disilabicyclo[4.4.0]deca-3,8-dienes and bi(benzo[*c*]silacyclopent-3-ene-1-yl)s

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## Abstract

The reaction of the di-Grignard reagent of  $\alpha,\alpha'$ -dichloro-*o*-xylene with  $\text{Cl}_2\text{RSiRCl}_2$  ( $\text{R} = \text{}^i\text{Pr}$  and  $\text{Me}$ ) produced *cis*-dibenzo[*c,h*]-1,6-dialkyl-1,6-disilabicyclo[4.4.0]deca-3,8-diene (**1**) and bi(benzo[*c*]-1-alkylsilacyclopent-3-ene-1-yl) (**2**). The structures of **1a** ( $\text{R} = \text{}^i\text{Pr}$ ) and **2a** ( $\text{R} = \text{}^i\text{Pr}$ ) were determined by X-ray crystallography. Crystal data for **1a**: orthorhombic, *Pbca*,  $a = 14.816(1)$ ,  $b = 16.263(1)$ ,  $c = 17.257(1)$  Å,  $V = 4158.1(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $R = 0.040$ ,  $R_w = 0.050$  for 2008 reflections. Crystal data for **2a**: triclinic,  $P\bar{1}$ ,  $a = 8.179(2)$ ,  $b = 10.389(3)$ ,  $c = 6.605(2)$  Å,  $\alpha = 100.39(2)^\circ$ ,  $\beta = 98.29(2)^\circ$ ,  $\gamma = 106.75(2)^\circ$ ,  $V = 517.0(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $R = 0.042$ ,  $R_w = 0.051$  for 1167 reflections. Compounds **1** and **2** have relatively low oxidation potentials (1.24–1.59 V *vs.* SCE, in acetonitrile) and form charge-transfer complexes with tetracyanoethylene (TCNE). In the case of **2a**, the charge-transfer complex was isolated as red crystals and the structure was determined by X-ray crystallography. Crystal data for the **2a**-TCNE complex: triclinic,  $P\bar{1}$ ,  $a = 6.8399(8)$ ,  $b = 8.2836(6)$ ,  $c = 12.868(1)$  Å,  $\alpha = 84.142(6)^\circ$ ,  $\beta = 88.737(6)^\circ$ ,  $\gamma = 66.801(8)^\circ$ ,  $V = 666.5(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $R = 0.038$ ,  $R_w = 0.042$  for 1554 reflections.

**Key words:** Silicon; Charge transfer

## 1. Introduction

As part of an ongoing investigation of the chemistry of polycyclopolysilanes [1–3], we have been interested in the construction of polycyclocarbopolysilanes in which strained Si–C or Si–Si bonds interact with carbon  $\pi$ -systems. Recently, synthesis and some unique properties of the bicyclic systems consisting of  $\sigma(\text{Si–Si})$ - $\pi$  conjugations have been reported by Iwahara and West [4] and Sakurai *et al.* [5]. We report here the synthesis of *cis*-dibenzo[*c,h*]-1,6-disilabicyclo[4.4.0]deca-3,8-diene and bi(benzo[*c*]silacyclopent-3-en-1-yl)s. Their structures, electronic properties and formation

of charge-transfer complexes are also described. A preliminary account of some aspects of this work has already appeared [6].

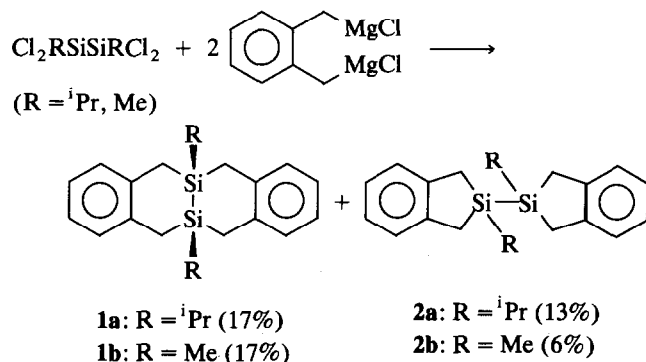
## 2. Results and discussion

### 2.1. Synthesis of *cis*-dibenzo[*c,h*]-1,6-disilabicyclo[4.4.0]deca-3,8-dienes and bi(benzo[*c*]silacyclopent-3-en-1-yl)s

The reaction of the di-Grignard reagent of  $\alpha,\alpha'$ -dichloro-*o*-xylene with 1,1,2,2-tetrachloro-1,2-diisopropylsilane afforded *cis*-dibenzo[*c,h*]-1,6-diisopropyl-1,6-disilabicyclo[4.4.0]deca-3,8-diene (**1a**) and bi(benzo[*c*]-1-isopropylsilacyclopent-3-en-1-yl) (**2a**) in 17% and 13% yields, respectively. Similarly, the reaction of the di-Grignard reagent with 1,1,2,2-tetrachloro-1,2-dimethyldisilane gave **1b** and **2b** in 17% and 6% yields,

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respectively. Although previously we assigned **2a** to be the stereoisomer of **1a** with a *trans* configuration on the basis of measurement of the NOE in  $^1\text{H}$  NMR [6], it has been proved by X-ray crystallography that the assignment was invalid (*vide infra*), and the *trans* isomer of **1** was not formed in the reaction mixture. The results are explained by the MM2 calculations [7] because the strain energy of **1** is far smaller than that of the *trans* isomer (**1a**:  $9.6\text{ kcal mol}^{-1}$ , the *trans* isomer of **1a**:  $20.4\text{ kcal mol}^{-1}$ ; **1b**:  $5.1\text{ kcal mol}^{-1}$ , the *trans* isomer of **1b**:  $16.2\text{ kcal mol}^{-1}$ ). Compounds **1** and **2** were easily separated by chromatography and were obtained as colourless crystals. Compounds **1a** and **2a** are relatively stable in air at room temperature, while **1b** and **2b** decompose within several days in air. As a consequence, it is indicated that the isopropyl substituents can serve as effective blockades against external attack.



## 2.2. Structures of **1a** and **2a**

The molecular structures of **1a** and **2a** are shown in Figs. 1 and 2. Crystallographic data, positional param-

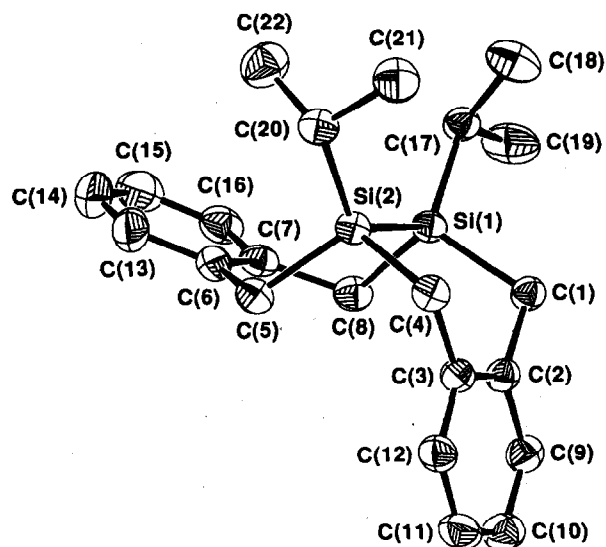


Fig. 1. ORTEP drawing of **1a**. Thermal ellipsoids are drawn at the 30% probability level.

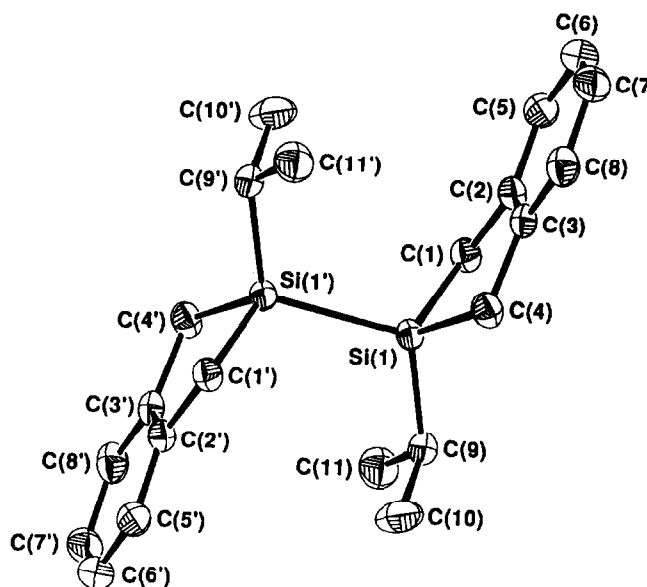


Fig. 2. ORTEP drawing of **2a** viewed along the *c* axis. Thermal ellipsoids are drawn at the 30% probability level.

eters and selected bond distances and angles are given in Tables 1–5.

Compound **1a** has a strained *cis*-fused bicyclic structure. The Si–Si bond distance is  $2.327(1)\text{ \AA}$ , which is among the shortest Si–Si distances yet reported (*cf.*  $\text{Me}_3\text{SiSiMe}_3$ :  $2.340(9)\text{ \AA}$  [8]; peripheral Si–Si bond of 1,3-di-*tert*-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)bicyclo[1.1.0]tetrasilane:  $2.308(3)\text{ \AA}$  [9]). The Si–Si–C(benzyl) angles ( $99.7(1)$ – $100.2(1)^\circ$ ) are smaller than the typical angle around  $\text{sp}^3$  silicon atoms. The distance between two benzyl carbon atoms of the *o*-xylylene groups is not long enough to connect the central Si–Si bond without distortion. The Si(1)–Si(2)–C(4)–C(3)–C(2)–C(1) and Si(1)–Si(2)–C(5)–C(6)–C(7)–C(8) rings have a boat conformation and two benzene rings are oriented in an *endo*, *exo* manner. In  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, it is shown that two benzene rings are equivalent. The result indicates that rapid flexing of the 1,6-disilabicyclo[4.4.0]deca-3,8-diene ring in the flip-flop motion occurs in a solution.

On the other hand, **2a** has a less strained structure (Fig. 2). The Si–Si bond distance ( $2.356(1)\text{ \AA}$ ) is normal. The silacyclopentene rings have an envelope conformation with the fold angle of  $24.6^\circ$ . The isopropyl group has an *anti*-conformation to the silacyclopentene ring, and the silacyclopentene ring is folded in the opposite direction of the isopropyl group so as to reduce the steric repulsion of the isopropyl groups.

Compounds **1a** and **2a** have four benzylsilane moieties in a molecule. It is known that the degree of  $\sigma$ - $\pi$  conjugation in benzylsilanes depends on the dihedral

angle between a Si–C(benzyl) bond and  $\pi$ -orbitals of a benzene ring [10]. The dihedral angles in the X-ray structure of **1a** are 28.5° (Si(1)–C(1)), 24.1° (Si(1)–C(8)), 29.2° (Si(2)–C(4)), and 26.8° (Si(2)–C(5)) with an average of 27.2°. In **2a**, the dihedral angles are 71.6° (Si(1)–C(1)) and 72.1° (Si(1)–C(4)) (Fig. 3). From these structures,  $\sigma$ - $\pi$  conjugation is considered to be more effective in the case of **1a**.

### 2.3. Electronic properties of 1 and 2

Compounds **1** and **2** have relatively low oxidation potentials [11\*]. However, the oxidation potentials de-

pend upon the structure. For example, compound **1a** is oxidized at 1.35 V *vs.* SCE in acetonitrile, whereas **2a** undergoes oxidation at 1.59 V *vs.* SCE. These results indicate that the highest occupied molecular orbital (HOMO) of **1a** is more destabilized than that of **2a** due to more effective  $\sigma$ - $\pi$  conjugation. A similar tendency is observed in **1b** ( $E_p^{\text{Ox}} = 1.24$  V *vs.* SCE) and **2b** ( $E_p^{\text{Ox}} = 1.47$  V *vs.* SCE), but these values are smaller

\* Reference number with asterisk indicates a note in the list of references.

TABLE 1. Summary of crystal data, data collection and refinement

	<b>1a</b>	<b>2a</b>	<b>2a-TCNE</b>
<i>Crystal data</i>			
Formula	C <sub>22</sub> H <sub>30</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>30</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>30</sub> Si <sub>2</sub> ·C <sub>6</sub> N <sub>4</sub>
Molecular weight	350.65	350.65	478.75
Crystal description	Colourless prisms	Colourless prisms	Red prisms
Crystal size (mm)	0.3 × 0.3 × 0.3	0.5 × 0.3 × 0.3	0.3 × 0.1 × 0.1
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.816(1)	8.179(2)	6.8399(8)
<i>b</i> (Å)	16.263(1)	10.389(3)	8.2836(6)
<i>c</i> (Å)	17.257(1)	6.605(2)	12.868(1)
$\alpha$ (°)		100.39(2)	84.142(6)
$\beta$ (°)		98.29(2)	88.737(6)
$\gamma$ (°)		106.75(2)	66.801(8)
<i>V</i> (Å <sup>3</sup> )	4158.1(3)	517.0(3)	666.5(1)
<i>Z</i>	8	1	1
<i>D</i> <sub>measd</sub> (mg m <sup>-3</sup> )	1.104	1.150	1.178
<i>D</i> <sub>calcd</sub> (mg m <sup>-3</sup> )	1.120	1.126	1.193
<i>Data collection</i>			
Diffractionmeter	Enraf-Nonius CAD-4	Rigaku AFC-6	Enraf-Nonius CAD-4
Radiation ( $\lambda$ (Å))	Cu K $\alpha$ (1.5418)	Mo K $\alpha$ (0.7107)	Cu K $\alpha$ (1.5418)
$\mu$ (mm <sup>-1</sup> )	2.0700	0.1669	1.2522
Absorption correction	None	None	None
Variation of standards	< 1%	< 1%	– 10.2%
2 $\theta$ range (°)	6–130	4–45	5–120
Range of <i>h</i>	0 to 17	– 8 to 8	– 7 to 7
<i>k</i>	0 to 19	– 11 to 11	– 9 to 9
<i>l</i>	0 to 20	0 to 7	0 to 14
Scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$
Scan width (°)	0.75 + 0.15tan $\theta$	1.3 + 0.50tan $\theta$	1.0 + 0.15tan $\theta$
No. of reflections measured	3534	1487	1957
No. of independent reflections	3534	1345	1957
No. of observed reflections ( $ F_o  \geq 3\sigma(F_o)$ )	2008	1167	1554
<i>Refinement</i>			
<i>R</i>	0.040	0.042	0.038
<i>R</i> <sub>w</sub>	0.050	0.051	0.042
Weighting scheme	$w = 1/[0.00286 F_o ^2 - 0.15307 F_o  + 3.28807]$	$w = 1/[\sigma^2(F_o) + 0.031571 F_o ^2]$	$w = 1/[0.00137 F_o ^2 - 0.01498 F_o  + 0.18594]$
<i>S</i>	1.929	0.413	0.524
( $\Delta/\sigma$ ) <sub>max</sub>	0.701	0.242	0.964
( $\Delta\rho$ ) <sub>max</sub> (e Å <sup>-3</sup> )	0.17	0.12	0.22
( $\Delta\rho$ ) <sub>min</sub> (e Å <sup>-3</sup> )	– 0.23	– 0.25	– 0.21
No. of parameters	337	169	214

TABLE 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for **1a**

Atom	x	y	z	$B_{\text{eq}}^a$ ( $\text{\AA}^2$ )
Si(1)	0.0773(1)	0.3153(1)	0.3738(1)	3.41(2)
Si(2)	-0.0211(1)	0.2404(1)	0.4518(1)	3.61(2)
C(1)	0.0659(3)	0.4201(2)	0.4193(2)	3.9(1)
C(2)	0.0743(2)	0.4182(2)	0.5060(2)	3.7(1)
C(3)	0.0136(2)	0.3738(2)	0.5526(2)	3.9(1)
C(4)	-0.0626(2)	0.3244(2)	0.5184(2)	4.3(1)
C(5)	0.0637(3)	0.1722(3)	0.5046(2)	4.6(1)
C(6)	0.1269(2)	0.1306(2)	0.4489(2)	4.5(1)
C(7)	0.1848(2)	0.1752(2)	0.4005(2)	4.2(1)
C(8)	0.1883(2)	0.2683(2)	0.4043(2)	4.3(1)
C(9)	0.1438(3)	0.4611(2)	0.5424(3)	4.6(1)
C(10)	0.1532(3)	0.4608(3)	0.6227(3)	5.5(1)
C(11)	0.0937(3)	0.4181(3)	0.6675(3)	5.7(1)
C(12)	0.0253(3)	0.3752(3)	0.6328(2)	4.9(1)
C(13)	0.1257(4)	0.0449(3)	0.4406(3)	6.1(1)
C(14)	0.1795(4)	0.0054(4)	0.3869(4)	7.4(2)
C(15)	0.2336(4)	0.0504(4)	0.3395(3)	7.2(2)
C(16)	0.2377(3)	0.1344(3)	0.3463(2)	5.5(1)
C(17)	0.0680(3)	0.3192(2)	0.2648(2)	4.2(1)
C(18)	-0.0245(4)	0.3452(5)	0.2374(3)	7.3(2)
C(19)	0.1421(4)	0.3727(5)	0.2300(3)	7.5(2)
C(20)	-0.1197(2)	0.1789(2)	0.4134(2)	4.5(1)
C(21)	-0.1960(3)	0.2335(3)	0.3852(3)	6.1(1)
C(22)	-0.0925(4)	0.1164(4)	0.3522(4)	7.0(2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as  $B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$ .

than those of **1a** and **2a**. The results are in accord with the observation that **1b** and **2b** easily decompose on standing in the air at room temperature, while **1a** and **2a** are relatively stable under the same conditions. Oxidation potentials are determined by both standard oxidation potentials and reorganization energies, and standard oxidation potentials of the isopropyl compounds and methyl compounds are considered to have quite close values by measurement of charge-transfer absorptions and UV spectra (*vide infra*). Therefore, the difference of the oxidation potentials of the isopropyl and methyl compounds might be attributable to the difference of reorganization energies. In this connection, it has been reported that the reorganization energies play an important role in oxidation potentials of organosilicon compounds [12].

In Fig. 4, UV spectra of **1b** and **2b** are shown. In **1b**, the  $^1L_a$  band extends to ca. 250 nm, and the  $^1L_b$  band appears at ca. 250–285 nm ( $\lambda_{\text{max}} = 280$  nm ( $\epsilon = 1780$ )). In **2b**, the  $^1L_a$  band has a shoulder at ca. 220 nm and the maximum wavelength of the  $^1L_b$  band is 277 nm ( $\epsilon = 1820$ ). It is noted that these absorptions show a bathochromic shift compared with benzene, and the degree of the shift is especially large in **1b**. The bathochromic shift is explained by the destabilization of the HOMO due to  $\sigma$ - $\pi$  conjugation. Since these

TABLE 3. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1a**

Bond distances			
Si(1)–Si(2)	2.327(1)	C(6)–C(13)	1.401(6)
Si(1)–C(1)	1.885(4)	C(7)–C(8)	1.516(6)
Si(1)–C(8)	1.888(4)	C(7)–C(16)	1.388(6)
Si(1)–C(17)	1.888(3)	C(9)–C(10)	1.393(6)
Si(2)–C(4)	1.889(4)	C(10)–C(11)	1.363(7)
Si(2)–C(5)	1.907(4)	C(11)–C(12)	1.368(7)
Si(2)–C(20)	1.892(4)	C(13)–C(14)	1.381(8)
C(1)–C(2)	1.501(5)	C(14)–C(15)	1.358(9)
C(2)–C(3)	1.406(5)	C(15)–C(16)	1.373(8)
C(2)–C(9)	1.394(5)	C(17)–C(18)	1.510(7)
C(3)–C(4)	1.506(5)	C(17)–C(19)	1.524(8)
C(3)–C(12)	1.395(5)	C(20)–C(21)	1.517(6)
C(5)–C(6)	1.504(6)	C(20)–C(22)	1.521(8)
C(6)–C(7)	1.400(5)		
Bond angles			
Si(2)–Si(1)–C(1)	100.1(1)	C(5)–C(6)–C(7)	122.0(3)
Si(2)–Si(1)–C(8)	100.0(1)	C(5)–C(6)–C(13)	120.3(4)
Si(2)–Si(1)–C(17)	123.3(1)	C(7)–C(6)–C(13)	117.6(4)
C(1)–Si(1)–C(8)	109.2(2)	C(6)–C(7)–C(8)	120.9(3)
C(1)–Si(1)–C(17)	112.2(2)	C(6)–C(7)–C(16)	120.0(4)
C(8)–Si(1)–C(17)	110.7(2)	C(8)–C(7)–C(16)	119.1(4)
Si(1)–Si(2)–C(4)	100.2(1)	Si(1)–C(8)–C(7)	111.2(2)
Si(1)–Si(2)–C(5)	99.7(1)	C(2)–C(9)–C(10)	121.3(4)
Si(1)–Si(2)–C(20)	123.9(1)	C(9)–C(10)–C(11)	120.2(4)
C(4)–Si(2)–C(5)	110.2(2)	C(10)–C(11)–C(12)	119.3(4)
C(4)–Si(2)–C(20)	110.1(2)	C(3)–C(12)–C(11)	122.4(4)
C(5)–Si(2)–C(20)	111.6(2)	C(6)–C(13)–C(14)	121.5(5)
Si(1)–C(1)–C(2)	112.9(2)	C(13)–C(14)–C(15)	119.7(5)
C(1)–C(2)–C(3)	121.8(3)	C(14)–C(15)–C(16)	120.7(5)
C(1)–C(2)–C(9)	120.0(3)	C(7)–C(16)–C(15)	120.6(4)
C(3)–C(2)–C(9)	118.2(3)	Si(1)–C(17)–C(18)	112.7(3)
C(2)–C(3)–C(4)	121.9(3)	Si(1)–C(17)–C(19)	111.1(3)
C(2)–C(3)–C(12)	118.7(3)	C(18)–C(17)–C(19)	111.7(4)
C(4)–C(3)–C(12)	119.4(3)	Si(2)–C(20)–C(21)	112.3(3)
Si(2)–C(4)–C(3)	112.3(3)	Si(2)–C(20)–C(22)	113.0(3)
Si(2)–C(5)–C(6)	111.5(3)	C(21)–C(20)–C(22)	111.5(4)

TABLE 4. Fractional atomic coordinates and equivalent isotropic thermal parameters for **2a**

Atom	x	y	z	$U_{\text{eq}}^a$ ( $\text{\AA}^2$ )
Si(1)	0.1259(1)	-0.0297(1)	-0.0221(1)	0.0364(4)
C(1)	0.2815(4)	0.0978(3)	-0.1352(4)	0.043(1)
C(2)	0.4071(3)	0.1982(3)	0.0583(4)	0.040(1)
C(3)	0.4109(3)	0.1536(3)	0.2461(4)	0.041(1)
C(4)	0.2885(4)	0.0114(3)	0.2348(5)	0.046(1)
C(5)	0.5122(4)	0.3302(3)	0.0603(5)	0.052(1)
C(6)	0.6184(4)	0.4171(3)	0.2432(6)	0.061(1)
C(7)	0.6235(5)	0.3743(4)	0.4307(6)	0.063(1)
C(8)	0.5197(4)	0.2417(3)	0.4310(5)	0.054(1)
C(9)	0.0811(4)	-0.2123(3)	-0.1726(5)	0.047(1)
C(10)	-0.0050(7)	-0.3204(4)	-0.0578(8)	0.075(2)
C(11)	-0.0152(6)	-0.2435(4)	-0.4002(6)	0.068(2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as  $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ .

TABLE 5. Bond distances (Å) and angles (°) for **2a**<sup>a</sup>

Bond distances			
Si(1')-Si(1')	2.356(1)	C(3)-C(4)	1.508(4)
Si(1)-C(1)	1.896(3)	C(3)-C(8)	1.391(4)
Si(1)-C(4)	1.894(3)	C(5)-C(6)	1.372(5)
Si(1)-C(9)	1.880(3)	C(6)-C(7)	1.388(5)
C(1)-C(2)	1.516(4)	C(7)-C(8)	1.395(5)
C(2)-C(3)	1.400(4)	C(9)-C(10)	1.528(5)
C(2)-C(5)	1.389(4)	C(9)-C(11)	1.523(5)
Bond angles			
Si(1')-Si(1)-C(1)	112.7(1)	C(2)-C(3)-C(8)	119.6(3)
Si(1')-Si(1)-C(4)	112.8(1)	C(4)-C(3)-C(8)	123.8(2)
Si(1')-Si(1)-C(9)	114.5(1)	Si(1)-C(4)-C(3)	103.8(2)
C(1)-Si(1)-C(4)	93.0(1)	C(2)-C(5)-C(6)	121.0(3)
C(1)-Si(1)-C(9)	111.0(1)	C(5)-C(6)-C(7)	120.4(3)
C(4)-Si(1)-C(9)	111.0(1)	C(6)-C(7)-C(8)	119.3(3)
Si(1)-C(1)-C(2)	103.5(2)	C(3)-C(8)-C(7)	120.5(3)
C(1)-C(2)-C(3)	116.5(2)	Si(1)-C(9)-C(10)	113.1(2)
C(1)-C(2)-C(5)	124.3(2)	Si(1)-C(9)-C(11)	114.1(2)
C(3)-C(2)-C(5)	119.2(3)	C(10)-C(9)-C(11)	111.9(3)
C(2)-C(3)-C(4)	116.5(2)		

<sup>a</sup> Primed atoms are generated by the crystallographic symmetry operator ( $-x, -y, -z$ ).

absorption bands, especially the <sup>1</sup>L<sub>a</sub> bands, reflect the degree of  $\sigma$ - $\pi$  conjugation, UV spectra also indicate more effective  $\sigma$ - $\pi$  conjugation in **1b**. The UV spectra of **1a** and **2a** are essentially the same as those of **1b** and **2b**, respectively [6]. Substituents on the silicon atoms of **1** and **2** have little effect on UV spectra.

#### 2.4. Formation of charge-transfer complexes of **1** and **2** with TCNE and the structure of the **2a**-TCNE complex

From the oxidation potentials of **1** and **2**, these compounds are expected to act as good electron donors. In fact, compounds **1** and **2** form charge-transfer complexes with tetracyanoethylene (TCNE). When **1** or **2** and TCNE are dissolved in dichloromethane, the solution immediately becomes purple (**1** and TCNE) or orange (**2** and TCNE). In UV-visible spectra, new absorption bands appear in the longer wavelength re-

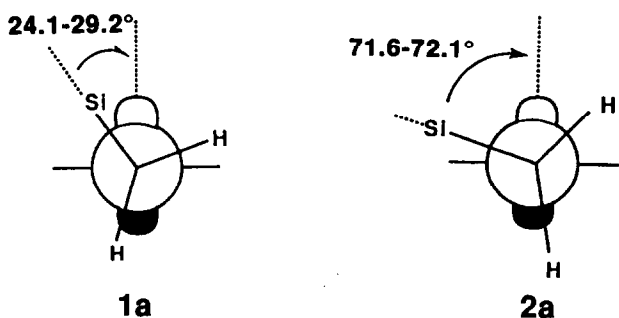


Fig. 3. Dihedral angles between the Si-C(benzyl) bonds and the  $\pi$ -orbitals of benzene rings in **1a** and **2a**.

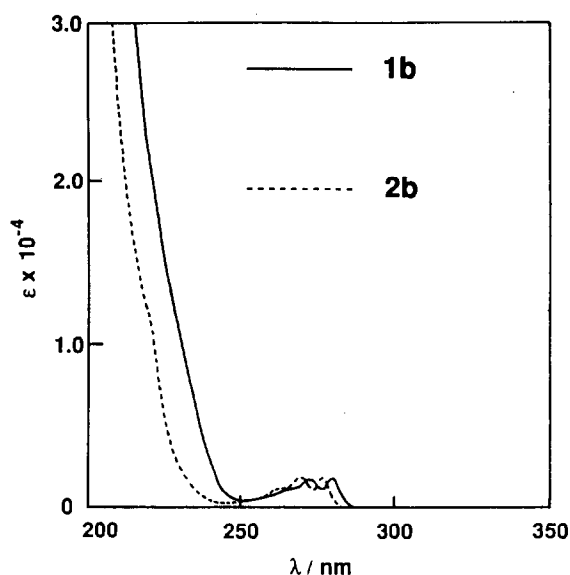


Fig. 4. UV spectra of **1b** and **2b** in hexane at room temperature.

gion (Fig. 5). Each absorption consists of two components and is simulated by skewed Gaussian lines [13] very well. Wavelengths and frequencies of the absorp-

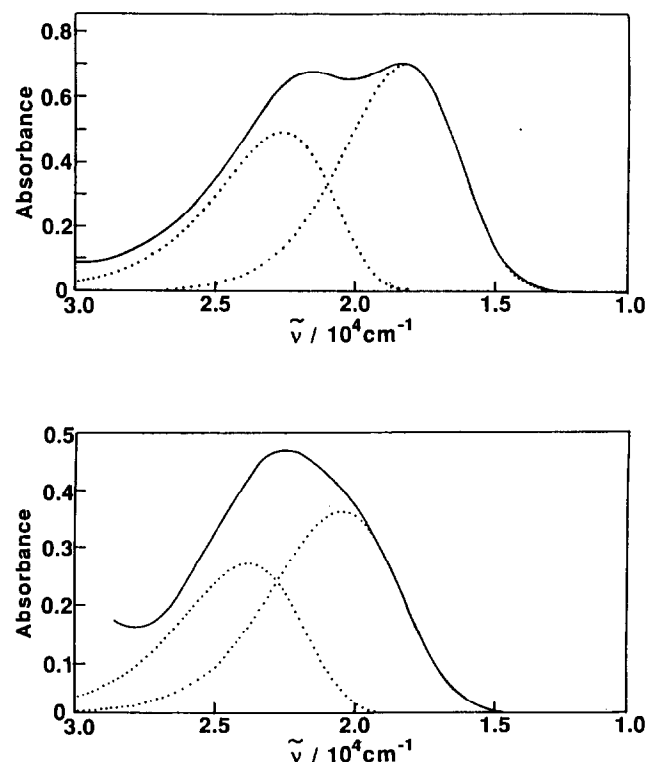


Fig. 5. Charge-transfer absorption spectra of **1b** (above) and **2b** (below) with TCNE in dichloromethane at room temperature. The concentrations of **1b**, **2b** and TCNE are 0.05, 0.05 and 0.005 M, respectively. Skewed Gaussian functions are represented by dotted lines.

TABLE 6. Frequencies for charge-transfer absorptions in complexes of **1** and **2** with TCNE in dichloromethane at room temperature

Compound	$\lambda_{\max}$ (CTI)/nm	$\tilde{\nu}_{\max}$ (CTI)/cm <sup>-1</sup>	$\lambda_{\max}$ (CTII)/nm	$\tilde{\nu}_{\max}$ (CTII)/cm <sup>-1</sup>
<b>1a</b>	448	22300	559	17900
<b>1b</b>	445	22500	554	18100
<b>2a</b>	422	23700	503	19900
<b>2b</b>	422	23700	493	20300

tion maxima are summarized in Table 6. The absorption bands of the charge-transfer complex of **1** and TCNE shift to a longer wavelength region than those of the **2**-TCNE complex. The result is in accord with Mulliken's charge-transfer theory [14] that the absorption band of a strong donor and a strong acceptor shifts to the longer wavelength region. No important difference of the charge-transfer absorption is observed between the isopropyl and methyl compounds.

Slow evaporation of a solution of **2a** and TCNE allowed crystallization of the charge-transfer complex. The crystals were obtained as red prisms and are stable in the air. X-ray crystallography confirmed the structure of the charge-transfer complex (Figs. 6 and 7). Crystallographic data, positional parameters and se-

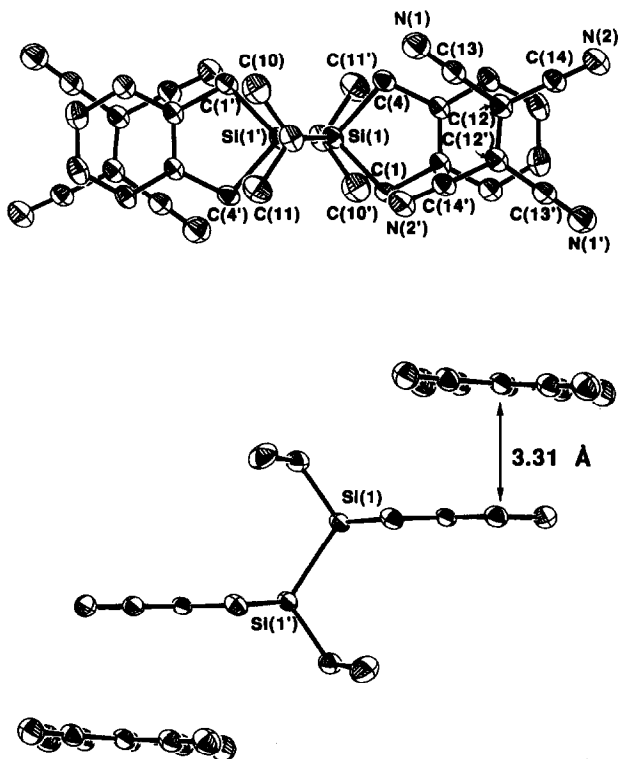


Fig. 6. Top view (above) and side view (below) of the molecular structure of the charge-transfer complex of **2a** and TCNE. The numbering of **2a** is identical with that of **2a** in Fig. 2. Thermal ellipsoids are drawn at the 30% probability level.

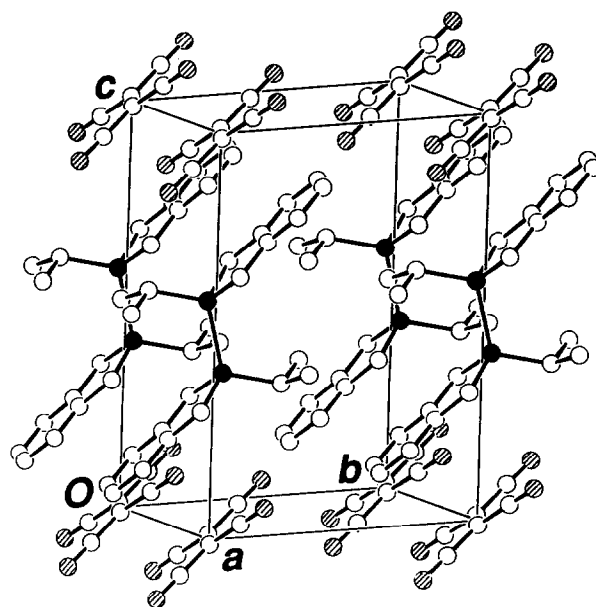


Fig. 7. Packing diagram of the charge-transfer complex of **2a** and TCNE projected on the *bc* plane. The filled circles denote silicon atoms. Nitrogen atoms are distinguished with the shades.

lected bond distances and angles are given in Tables 1, 7 and 8. The complex is composed of **2a** and TCNE in 1:1 ratio. The benzene rings of **2a** interact with two TCNE molecules in the parallel stacking manner with the distance of 3.31 Å. Therefore, the charge-transfer absorption bands which appeared in the UV-visible spectra are explained by the interaction of the benzene

TABLE 7. Fractional atomic coordinates and equivalent isotropic thermal parameters for **2a**-TCNE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}^a$ (Å <sup>2</sup> )
Si(1)	-0.0065(1)	0.0347(1)	0.4087(1)	3.31(2)
C(1)	0.2284(4)	-0.1215(4)	0.3387(2)	3.8(1)
C(2)	0.1348(4)	-0.2107(3)	0.2695(2)	3.2(1)
C(3)	-0.0876(4)	-0.1567(3)	0.2691(2)	3.3(1)
C(4)	-0.2124(4)	-0.0159(4)	0.3384(2)	3.8(1)
C(5)	0.2561(5)	-0.3424(3)	0.2082(2)	3.9(1)
C(6)	0.1619(5)	-0.4212(4)	0.1479(2)	4.7(1)
C(7)	-0.0568(5)	-0.3674(4)	0.1471(2)	4.8(1)
C(8)	-0.1795(5)	-0.2361(4)	0.2062(2)	4.0(1)
C(9)	-0.0403(5)	0.2694(4)	0.3690(2)	4.5(1)
C(10)	-0.2509(7)	0.4032(5)	0.4042(4)	6.4(1)
C(11)	0.1459(7)	0.3091(5)	0.4027(4)	6.3(1)
C(12)	-0.1071(4)	0.0333(3)	0.0022(2)	3.9(1)
C(13)	-0.2183(4)	0.1790(4)	0.0615(2)	4.1(1)
C(14)	-0.2280(4)	-0.0394(4)	-0.0540(2)	4.2(1)
N(1)	-0.3043(4)	0.2950(4)	0.1081(2)	5.6(1)
N(2)	-0.3239(4)	-0.0956(4)	-0.0978(2)	5.7(1)

<sup>a</sup> Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as  $B_{\text{eq}} = (4/3)\sum_i \Sigma_j \beta_{ij} a_i a_j$ .

TABLE 8. Bond distances (Å) and angles (°) for **2a**-TCNE<sup>a</sup>

<i>Bond distances</i>			
Si(1)–Si(1')	2.356(1)	C(6)–C(7)	1.382(5)
Si(1)–C(1)	1.899(3)	C(7)–C(8)	1.374(4)
Si(1)–C(4)	1.892(3)	C(9)–C(10)	1.524(5)
Si(1)–C(9)	1.882(3)	C(9)–C(11)	1.518(6)
C(1)–C(2)	1.510(5)	C(12)–C(13)	1.434(4)
C(2)–C(3)	1.406(4)	C(12)–C(14)	1.441(5)
C(2)–C(5)	1.391(3)	C(12)–C(12')	1.349(4)
C(3)–C(4)	1.509(3)	C(13)–N(1)	1.134(4)
C(3)–C(8)	1.393(4)	C(14)–N(2)	1.129(5)
C(5)–C(6)	1.379(5)		
<i>Bond angles</i>			
Si(1')–Si(1)–C(1)	114.0(1)	Si(1)–C(4)–C(3)	105.4(2)
Si(1')–Si(1)–C(4)	114.2(1)	C(2)–C(5)–C(6)	121.1(3)
Si(1')–Si(1)–C(9)	113.1(1)	C(5)–C(6)–C(7)	119.7(3)
C(1)–Si(1)–C(4)	94.8(1)	C(6)–C(7)–C(8)	120.1(3)
C(1)–Si(1)–C(9)	109.7(1)	C(3)–C(8)–C(7)	121.2(3)
C(4)–Si(1)–C(9)	109.8(1)	Si(1)–C(9)–C(10)	112.5(3)
Si(1)–C(1)–C(2)	105.3(2)	Si(1)–C(9)–C(11)	113.1(2)
C(1)–C(2)–C(3)	117.2(2)	C(10)–C(9)–C(11)	111.3(3)
C(1)–C(2)–C(5)	123.6(2)	C(13)–C(12)–C(14)	118.9(2)
C(3)–C(2)–C(5)	119.2(3)	C(13)–C(12)–C(12')	120.6(3)
C(2)–C(3)–C(4)	117.4(3)	C(14)–C(12)–C(12')	120.5(2)
C(2)–C(3)–C(8)	118.7(2)	C(12)–C(13)–N(1)	179.2(4)
C(4)–C(3)–C(8)	123.9(2)	C(12)–C(14)–N(2)	179.6(3)

<sup>a</sup> Primed atoms are generated by the crystallographic symmetry operator ( $-x, -y, -z$ ).

ring of **2a** with TCNE. The presence of two bands in the spectra is demonstrated by separation of the degenerate HOMO's of the benzene ring by the  $\sigma$ - $\pi$  conjugation [6]. It is interesting to compare the structural change of **2a** before and after complexation with TCNE. Such investigation has not yet been reported in spite of many studies on the charge-transfer complex of benzylsilanes in solution [15]. Interestingly, the structure of the silacyclopentene ring in the **2a**-TCNE complex is planar. The planar structure is quite different from the envelope structure with the fold angle of 24.6° in isolated **2a**. The origin of the structural change in **2a** is not clear at this moment. It may be due to the effect of the partial charge on **2a** or due to the molecular packing in the unit cell.

### 3. Experimental details

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Benzene was distilled from lithium aluminium hydride. Acetone was distilled from anhydrous calcium sulfate. Acetonitrile was distilled from calcium hydride. Hexane and methanol were distilled. Hydrogen chloride was passed through sulfuric acid before use. Aluminium chloride and TCNE sublimed before use.  $\alpha, \alpha'$ -Dichloro-*o*-xylene was recrystallized from hexane. 1,1,2,2-Tetrachloro-1,2-diisopropyl-

pyldisilane [4], 1,1,2,2-tetrachloro-1,2-dimethyldisilane [16] and the di-Grignard reagent of  $\alpha, \alpha'$ -dichloro-*o*-xylene [17] were prepared by published procedures. Tetrabutylammonium perchlorate was dried under reduced pressure at room temperature. IR spectra were recorded on a JASCO A-102 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a Varian Gemini-200 spectrometer. Mass spectra were recorded on a JEOL JMS-DX302 mass spectrometer. UV spectra were obtained with a JASCO Ubest-50 spectrophotometer. Oxidation potentials were measured by cyclic voltammetry in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte by using a saturated calomel electrode (SCE) as a reference under deaerated conditions. Elemental analyses were performed by the Institute of Physical and Chemical Research.

#### 3.1. Reaction of 1,1,2,2-tetrachloro-1,2-diisopropylidisilane with the di-Grignard reagent of $\alpha, \alpha'$ -dichloro-*o*-xylene

To the di-Grignard reagent of  $\alpha, \alpha'$ -dichloro-*o*-xylene (0.0765 M, 390 ml), a solution of 1,1,2,2-tetrachloro-1,2-diisopropylidisilane (3.52 g, 12.4 mmol) in THF (50 ml) was added during 1.5 h at room temperature. The reaction mixture was stirred for an additional 46 h at room temperature. After hydrolysis, hexane was added and the organic layer was washed repeatedly with water and dried over anhydrous sodium sulfate. By evaporation of the solvent, 4.836 g of a solid was obtained. A part of the solid (1.779 g) was briefly separated by thin-layer chromatography on silica gel (eluent: hexane/benzene = 9/1) to give 0.730 g of a mixture. 0.490 g of the mixture was subjected to recycle-type HPLC (ODS, eluent: methanol/THF = 8/2) to give dibenzo[*c,h*]-1,6-diisopropyl-1,6-disilabicyclo[4.4.0]deca-3,8-diene (**1a**) (0.184 g, 0.525 mmol) and bi(benzo[*c*]-1-isopropylsilacyclopent-3-en-1-yl) (**2a**) (0.145 g, 0.414 mmol) as colourless crystals. The calculated yields of **1a** and **2a** are 17% and 13%, respectively.

**1a**: m.p. 49.0–51.5°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.96–1.10 (m, 14H), 1.85 (d, 4H,  $J = 13.6$  Hz), 2.20 (d, 4H,  $J = 13.6$  Hz), 6.93–7.06 (m, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  11.4, 19.1, 19.6, 125.1, 129.6, 138.1. IR (KBr, cm<sup>-1</sup>): 1490, 1471, 1459, 1217, 1155, 779. MS:  $m/z$  350 (100, M<sup>+</sup>), 307 (65), 265 (89). HRMS. Found: 350.1883. C<sub>22</sub>H<sub>30</sub>Si<sub>2</sub> calc.: 350.1886.

**2a**: m.p. 50.0–52.0°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.96–1.15 (m, 14H), 2.08 (d, 4H,  $J = 17.4$  Hz), 2.21 (d, 4H,  $J = 17.4$  Hz), 7.03 (dd, 4H,  $J = 5.5, 3.4$  Hz), 7.17 (dd, 4H,  $J = 5.5, 3.4$  Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.2, 18.0, 18.8, 125.6, 128.8, 142.5. IR (KBr, cm<sup>-1</sup>): 1486, 1471, 1460, 1217, 1124, 790. MS:  $m/z$  350 (63, M<sup>+</sup>), 307

(100), 265 (96). Anal. Found: C, 75.15; H, 8.65.  $C_{22}H_{30}Si_2$  calc.: C, 75.36; H, 8.62%.

### 3.2. Reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with the di-Grignard reagent of $\alpha, \alpha'$ -dichloro-*o*-xylene

To the di-Grignard reagent of  $\alpha, \alpha'$ -dichloro-*o*-xylene (0.069 M, 450 ml), a solution of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (3.08 g, 13.5 mmol) in THF (50 ml) was added during 1.7 h at room temperature. The reaction mixture was stirred for 29 h at room temperature. After hydrolysis, the organic layer was dried over anhydrous sodium sulfate and the solvent was removed by evaporation. The resulting mixture was briefly separated by preparative TLC on silica gel (eluent: hexane/benzene = 8/2), and the product was isolated by recycle-type HPLC (ODS, eluent: methanol). Dibenzo- $[c, h]$ -1,6-dimethyl-1,6-disilabicyclo[4.4.0]deca-3,8-diene (**1b**) (0.676 g, 2.30 mmol) and bi(benzo[*c*]-1-methylsilacyclopent-3-en-1-yl) (**2b**) (0.237 g, 0.805 mmol) were obtained as colourless crystals in 17% and 6% yields, respectively.

**1b**: m.p. 95.0–96.5°C.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.07 (s, 6H), 1.96 (d, 4H,  $J = 13.5$  Hz), 2.14 (d, 4H,  $J = 13.5$  Hz), 6.99 (s, 8H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  8.0, 22.4, 125.2, 129.5, 137.8. IR (KBr,  $cm^{-1}$ ): 1480, 1450, 1408, 1208, 1135, 780. MS:  $m/z$  294 (57,  $M^+$ ), 279 (8), 146 (100). Anal. Found: C, 74.49; H, 7.66.  $C_{18}H_{22}Si_2$  calc.: C, 74.40; H, 7.53%.

**2b**: m.p. 32.0–32.5°C.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.25 (s, 6H), 2.10 (d, 4H,  $J = 17.0$  Hz), 2.21 (d, 4H,  $J = 17.0$  Hz), 7.06 (dd, 4H,  $J = 5.5, 3.3$  Hz), 7.20 (dd, 4H,  $J = 5.5, 3.3$  Hz).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  4.4, 20.2, 125.6, 128.9, 142.2. IR (KBr,  $cm^{-1}$ ): 1478, 1460, 1455, 1285, 1250, 1170, 1120, 740. MS:  $m/z$  294 (55,  $M^+$ ), 279 (8), 146 (100). HRMS. Found: 294.1257.  $C_{18}H_{22}Si_2$  calc.: 294.1260.

### 3.3. X-ray crystallographic analysis of **1a** and the charge-transfer complex of **2a** with TCNE

Colourless crystals of **1a** were obtained from a methanol solution by slow evaporation. Red crystals were grown from a dichloromethane solution of **2a** and TCNE (1:1) by slow evaporation. These crystal specimens were sealed in glass capillaries and used for data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu  $K\alpha$  radiation. Cell parameters were refined by the least-squares method using 25 reflections with  $26 < 2\theta < 40^\circ$  in the case of **1a** and 22 reflections with  $20 < 2\theta < 55^\circ$  in the case of the **2a**-TCNE complex. Intensity data were collected in the range of  $6 < 2\theta < 130^\circ$  by the  $\omega$ - $2\theta$  scan technique (**1a**) and in the range of  $5 < 2\theta < 120^\circ$  by the  $\omega$  scan technique (**2a**-TCNE) at room temperature. Three standard reflections were measured after every 1 h,

showing no decay in **1a**, and varied less than 10.2% in the **2a**-TCNE complex. The structure was solved by direct methods using MULTAN78 [18]. Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using UNICSII [19]. In the case of **1a**, 28 hydrogen atoms were located from difference Fourier and the remaining hydrogen atoms were located at calculated positions. In the case of the **2a**-TCNE complex, all hydrogen atoms were located from difference Fourier synthesis. All hydrogen atoms were refined isotropically. Atomic scattering factors were taken from ref. 20. All calculations were carried out on a FACOM M-380 computer. Details of crystal data, data collection and refinement are listed in Table 1.

### 3.4. X-ray crystallographic analysis of **2a**

Colourless crystals of bi(benzo[*c*]-1-isopropylsilacyclopent-3-en-1-yl) were obtained from a methanol solution by slow evaporation. A crystal specimen was sealed in a glass capillary and used for data collection on a Rigaku AFC-6 diffractometer using graphite-monochromated Mo  $K\alpha$  radiation. Cell parameters were refined by the least-squares method using 20 reflections with  $14 < 2\theta < 26^\circ$ . Intensity data were collected in the range of  $4 < 2\theta < 45^\circ$  by the  $\omega$ - $2\theta$  scan technique at room temperature. Three standard reflections were measured after every 100 reflections, showing no decay. The structure was solved by direct methods using SHELXS86 [21]. Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using SHELX76 [22]. All hydrogen atoms were located from difference Fourier synthesis and refined isotropically. Atomic scattering factors were taken from ref. 20. All calculations were carried out on a HITAC M-682H computer. Details of crystal data, data collection and refinement are listed in Table 1.

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